

## REMARKS

Claims 1, 4, 7, 10, 13 and 16-25 are presently pending in this application.

### *Allowable Subject Matter*

On page 8, paragraph 10 of the Office Action (Paper No. 9), the Examiner has stated that claims 16-25 are objected to as being dependent upon a rejected base claim, but would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims. On page 9 of Paper No. 9, the Examiner provides a reason for allowance stating that "...none of the prior art of record appears to teach, suggest or render obvious, the invention of claims 16 and 21." Although Applicants respectfully disagree, the Examiner contends that JP 11-219701 ("JP '701") teaches a positive electrode having a first and second active materials in the relationship defined by claim 1. However, the Examiner acknowledges that there is no teaching or suggestion to further add cobalt hydroxide or cobalt oxyhydroxide in combination with the relationships set forth in respective claims 16 and 21. The Examiner also acknowledges that the prior art of record does not appear to teach or suggest a combination of cobalt hydroxide or cobalt oxyhydroxide mixed with first and second active materials bound by the constituents of the relationships in respective claims 16 and 21. Further, the Examiner finds that, since claims 17-20 and 22-25 are dependent upon claims 16 and 21, respectively, those claims are also allowable.

Applicants thank the Examiner for this statement of allowable subject matter. However, at this time, Applicants have elected not to rewrite claims 16-25 in independent form as Applicants strongly believe that independent claim 1, from which they directly or indirectly depend, is allowable for the reasons set forth below.

**Rejection Under 35 U.S.C. § 103(a) Based On JP '701 and JP '508**

The Examiner has rejected claims 1 and 4 under 35 U.S.C. § 103(a) as being unpatentable over JP '701 in view of JP 08-203508-A ("JP '508") (an English translation of which is attached hereto as Exhibit A). As in the previous Office Action (Paper No. 4), the Examiner once again argues in Paper No. 9 that JP '701 discloses a positive electrode for an alkaline storage battery containing a first active material and a second active material where the first active material comprises X parts by weight of nickel hydroxide (X being 90-60 weight percent of the first and second active materials) with  $aX/100$  parts by weight of cobalt oxyhydroxide ( $aX/100$  being 1-10 weight percent of cobalt oxyhydroxide), and the second active material comprises Y parts by weight of particulate nickel oxyhydroxide (Y being 10-40 weight percent of the first and second active materials) and  $bX/100$  parts by weight of cobalt oxyhydroxide ( $bX/100$  being 1-10 weight percent of cobalt hydroxide). The Examiner contends that the nickel in the second active material has an inherent oxidation number  $\alpha$  and that one of the nickel hydroxide and nickel oxyhydroxide contains at least one of cobalt, zinc, cadmium, magnesium, calcium, manganese, and aluminum.

The Examiner acknowledges that JP '701 does not explicitly disclose the oxidation number of the nickel in the second active material to be from 2.6 to 2.92. However, in Paper No. 9, the Examiner contends that JP '508 discloses that nickel valence levels from 2.2-3.4 are known and that JP '508 also cites a specific value of 2.8. Therefore, the Examiner argues that selection of a nickel valence level between 2.2-3.4 encompasses the instant claimed range, and that the specific value of 2.8 is also within the instant claimed range.

Further, the Examiner argues that the motivation for selecting the nickel valence of JP '701 to be from 2.6 to 2.92 is that it optimizes the charge and discharge cycle of the electrochemical cell. The Examiner concludes that it would have been obvious to one of

ordinary skill in the art at the time the claimed invention was made to modify the teachings of JP '701 by selecting the nickel valence of JP '701 to be from 2.6 to 2.92, since it would have optimized the charge and discharge cycle of the electrochemical cell. Applicants respectfully traverse this rejection as follows.

The combination of JP '508 and JP '701 does not lead to the structure of the present invention nor is there any motivation to combine the teachings of JP '508 and JP '701 in the manner suggested by the Examiner. Although JP '508 teaches adding a nickel compound having a nickel valence of 2.2 to 3.4 to a negative electrode of an alkaline storage battery, it does not teach or suggest the relation between the amount of the oxidizing agent and the valence of nickel oxyhydroxide as recited in claim 1. Moreover, neither JP '701 nor JP '508 teaches or suggests the preferred range of the mean valence of nickel represented by equation (4) of the present claims. For example, since JP '701 does not disclose the valence of nickel in the second active material, it would not be obvious based on this reference to regulate the mean valence of nickel contained in the whole active material, as described at page 5, line 16 to page 6, line 11 of the specification, or to regulate the amount of the discharge reservoir of the negative electrode to a proper level. Therefore, based on the proposed combination, it would not have been obvious to one skilled in the art how to obtain a low-cost battery with a high capacity and a long cycle life which has the claimed characteristics.

Further, like the present invention, JP '701 relates, generally, to a non-sintered type (paste type) nickel **positive** electrode for an alkaline storage battery. In contrast, JP '508 relates to a cadmium **negative** electrode plate for a nickel-cadmium storage battery (see, e.g., JP '508 at ¶ [0001]. According to JP '508, a battery's life cycle is increased by adding a nickel compound having a nickel valence of 2.2 to 3.4 to a negative electrode (see, e.g., JP '508 at ¶¶ [0004] and [0006]). Thus, the nickel compound is used as an additive for improving the negative

electrode of the storage battery, which is irrelevant to the improvements of the positive electrodes of both JP '701 and the present invention.

Since the structure, characteristics and operation of a negative electrode in an alkaline storage battery are different from those of a positive electrode, techniques employed for improving a negative electrode are not necessarily the same as or even applicable toward improving a positive electrode (see, e.g., page 3, line 1 to page 6, line 11 of the present specification). As a result, while an argument could be made, for example, that there is a motivation to apply the teaching of JP '508 to improve a negative electrode of an alkaline battery, there is no motivation to modify the positive electrode described in JP '701 based on the teachings of JP '508. Besides, there is no suggestion to modify and/or to combine JP '701 and JP '508 in the manner suggested by the Examiner in either of the cited references. Thus, there is also no reasonable expectation of success from such a motivation and/or combination. Applicants have surprisingly found that the paste type positive electrode recited in, for example, claim 1 provides a battery having improved energy density and a lower manufacturing cost (page 5, lines 2-6). It was only through extensive investigation and inventive activity that Applicants discovered the claimed positive electrode having the appropriate oxidation number range for nickel.

Notwithstanding, even if *prima facie* obviousness could be shown based on the above-noted combination of references, such *prima facie* obviousness is sufficiently overcome by Applicants' improved and unexpected results. Specifically, Applicants have demonstrated that the amount of the discharge reservoir of the negative electrode can be optimized by regulating the mean valence of nickel in the positive electrode. As a result, it is possible to reduce the amount of expensive hydrogen storage alloy to be used, thus enabling the production of a low-cost battery with a high energy density (page 31, lines 6 to 11). For example, a battery

with a discharge reservoir of not greater than 10% (such as recited in claim 13 and described at page 27, line 17 to page 28, line 16 and in Tables 1 and 2) can be produced. As shown in Tables 1 and 2, the batteries according to the present invention (1, 2, and 3) exhibited favorable properties relative to the comparative examples, which is due in part to the difference in oxidation number of nickel in the positive electrodes. It is noted that Comparative Example 13 is the example from JP '701, which is clearly inferior to the presently claimed electrodes. This demonstrates the superiority of the present invention over the prior art.

For all of these reasons, the Examiner's rejection based on the proposed combination of JP '701 and JP '508 is improper, and reconsideration and withdrawal of the § 103(a) rejection are respectfully requested.

**Rejection Under 35 U.S.C. § 103(a) Based on JP '701, JP '508, and Kato**

The Examiner has rejected claim 7 under § 103(a) as being unpatentable over JP '701 in view of JP '508 as applied to claims 1 and 4 above, and in further view of U.S. Patent No. 6,083,642 of Kato for the same reasons provided in Paper No. 4. The Examiner acknowledges that JP '701 and JP '508 do not teach that the oxidation number of the cobalt in the oxyhydroxide in the active materials is greater than 3. However, the Examiner argues that Kato discloses a process in which the nickel active material is coated with cobalt having an oxidation number greater than 3, and that using a higher valence cobalt material provides a positive electrode material having high active material utilization and improved overdischarge withstanding characteristics. Therefore, the Examiner concludes that it would have been obvious to one of ordinary skill in the art at the time of the invention to modify the teachings of JP '701 by providing a higher valence cobalt material to provide such favorable properties. Applicants respectfully traverse this rejection as follows.

The argument with respect to claims 1 and 4 above are equally applicable here. In addition, as Applicants argued in the their previous Amendment filed March 31, 2003, there are several reasons for utilizing cobalt oxyhydroxide having a cobalt valence greater than 3 in the claimed active materials. First, since the valence of cobalt can change to 3 during charge/discharge cycles, if the valence of cobalt is initially less than 3, a discharge reservoir, which is undesirable for the negative electrode, is produced while the valence of cobalt changes to 3 in the battery. On the other hand, when cobalt oxyhydroxide with a valence of cobalt of greater than 3 is used initially, the valence of cobalt does not change and such excessive discharge reservoir can be eliminated. In addition, since cobalt oxyhydroxide with a valence of cobalt of greater than 3 is very stable throughout the long cycle of charge/discharge, it is possible to accurately set the discharge reservoir.

Further, the second active material can be obtained efficiently by further subjecting the first active material to an oxidation treatment. However, if the valence of cobalt in the surface layer of the first active material is 3, the utilization rate of the second active material obtained from oxidation of the first active material will be low compared with the utilization rate of the first active material before oxidation. On the contrary, if the valence of cobalt in the surface layer is greater than 3, specifically, 3.12 or 3.19, the second active material utilization rate is almost the same as that before oxidation, because the cobalt compound having a cobalt valence greater than 3 has a more stable structure in which alkali cations are intercalated between the layers.

In summary, the use of cobalt oxyhydroxide with a valence of cobalt of greater than 3 used in claim 7 eliminates the excessive discharge reservoir due to the valence change of cobalt, avoids the variations in the discharge reservoir, and prevents the second active material utilization rate from decreasing.

Kato teaches coating nickel active material with cobalt having an oxidation number greater than 3 for providing a high active material utilization rate and improved overdischarge withstanding characteristics. However, Kato does not teach or suggest that regulating the valence of cobalt in cobalt oxyhydroxide would additionally stabilize the cobalt oxyhydroxide, which significantly affects and optimizes the discharge reservoir. Accordingly, it would not have been expected based on the proposed combination that to apply cobalt oxyhydroxide with a valence of cobalt of greater than 3 to JP '701, combined with regulating the mean valence of nickel contained in the positive electrode as claimed, would eliminate the excessive discharge reservoir due to the valence change of cobalt and avoid the variations in the discharge reservoir. For these reasons, no *prima facie* case of obviousness has been established by the Examiner, and reconsideration and withdrawal of the § 103(a) rejection based on JP '701, JP '508 and Kato are respectfully requested.

**Rejection Under 35 U.S.C. § 103(a) Based on JP '701, JP '508, and Ikoma**

The Examiner has rejected claims 10 and 13 under § 103(a) as being unpatentable over JP '701 in view of JP '508 as applied to claims 1 and 4 above, and in further view of U.S. Patent No. 4,837,119 of Ikoma. The Examiner acknowledges that JP '701 and JP '508 do not teach that the battery further comprises a negative electrode comprising a hydrogen storage alloy, a separator, an aqueous alkaline electrolyte solution, a sealing plate having a safety valve and a battery case as claimed. However, the Examiner, making the same arguments as presented in Paper No. 4, contends that such modifications of the overall components of the battery would have been readily apparent. Further, the Examiner argues that Ikoma discloses a sealed storage battery comprising a positive electrode, negative electrode, separator, aqueous electrolyte solution, and a sealing plate having a safety valve. In order to measure the performance of the

cells of JP '701 having positive electrodes, the presence of an opposing negative electrode is allegedly required, as well as an electrolyte solution to enable charge transfer in the battery, and Ikoma allegedly teaches the use of a positive electrode, negative electrode, and aqueous alkaline electrolyte solution. Therefore, the Examiner concludes that it would have been obvious to one of ordinary skill in the art at the time of the invention to modify the teachings of JP '701 by providing a negative electrode and electrolyte solution to effectively enable charge transfer from the positive electrode to a second electrode across the electrolytic medium.

The Examiner also argues, as he did in Paper No. 4, that it would have been obvious to modify JP '701 by using a separator, allegedly an obvious addition in manufacturing a cell, to electrically isolate the positive and negative electrode materials. Regarding the sealing plate, which is allegedly taught by Ikoma to seal the battery components from the external atmosphere, the Examiner argues that it would have been obvious to modify JP '701 by providing a sealing plate to the open end of a battery since it would have sealed the battery components within the battery and isolated them from the external environment. Finally, the Examiner argues that Ikoma describes providing a safety valve in the sealing plate which releases the gas generated in the battery when the inner pressure rises above a given value in order to prevent damage to the battery and explosion in case of abnormal increase of internal pressure. Therefore, the Examiner concludes that it would have been obvious to modify JP '701 by providing a safety valve in the sealing plate to compensate for internal pressure fluxes. Applicants respectfully traverse this rejection as follows.

Applicants once again point out that Ikoma teaches a sealed storage battery comprising a positive electrode, a negative electrode, an alkaline electrolyte, a separator, and a sealing plate having a safety valve. However, the storage battery recited in the present claims 10 and 13 has a paste type positive electrode according to claim 1. As previously explained, neither



JP '701, JP '508 nor their combination teaches or suggests all of the elements of claim 1, and Ikoma does not cure these deficiencies. Further, claim 13 refers to the discharge capacity of the negative electrode as being 1 to 1.1 times larger than that of the positive electrode. None of the cited references teaches or suggests these claimed discharge properties.

For these reasons, no *prima facie* case of obviousness has been established based on the proposed combination of JP '701, JP '508 and Ikoma, and reconsideration and withdrawal of the § 103(a) rejection are respectfully requested.

In view of the foregoing Remarks, Applicants submit that pending claims 1, 4, 7, 10 and 13, in addition to claims 16-25, are not *prima facie* obvious over and/or in view of the cited prior art but, instead, are patentably distinct from the prior art. Accordingly, reconsideration and withdrawal of the Examiner's § 103(a) rejections, and an early Notice of Allowance are respectively requested.

Respectfully submitted,

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9/17/03  
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Laid-Open Patent Publication No. HEI8-203508

[TITLE OF THE INVENTION]

PASTE TYPE CADMIUM NEGATIVE ELECTRODE PLATE FOR ALKALINE  
STORAGE BATTERY AND METHOD OF MANUFACTURING THE SAME

[CLAIMS]

[Claim 1] A paste type cadmium negative electrode plate for an alkaline storage battery comprising a paste type active material added with a nickel compound, wherein

the nickel compound includes a nickel compound which is electrochemically produced from  $\text{Ni}(\text{OH})_2$  as a raw material to have a nickel valence of 2.2 to 3.4.

[Claim 2] The paste type cadmium negative electrode plate for an alkaline storage battery in accordance with claim 1, wherein the nickel compound contains at least one of  $\text{NiOOH}$  and  $\text{NiO}_2$ .

[Claim 3] The paste type cadmium negative electrode plate for an alkaline storage battery in accordance with claim 2, wherein the content of the nickel compound with respect to the paste type active material is 0.05 to 1.0 wt%.

[Claim 4] A method of manufacturing a paste type cadmium negative electrode plate for an alkaline storage battery comprising filling an active material paste added with  $\text{Ni}(\text{OH})_2$  in a current collector, wherein

an unformed electrode plate in which an active material paste added with  $\text{Ni}(\text{OH})_2$  is filled in a current

collector is formed and then overdischarged until a nickel valence thereof reaches 2.2 to 3.4.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[FIELD OF INDUSTRIAL APPLICATION]

The present invention relates to a paste type cadmium negative electrode plate for an alkaline storage battery and a method of manufacturing the same.

[0002]

[PRIOR ART]

A paste type cadmium negative electrode plate used for an alkaline storage battery is made by filling an active material paste in a current collector such as nickel punched metal. When an alkaline storage battery using a negative electrode plate of this kind is charged and discharged repetitively, a problem occurs in that cadmium as the active material coagulates to decrease the discharge capacity as compared with a sintered type alkaline storage battery. Hence, as shown in Japanese Laid-Open Patent Publication No. HEI2-189863, it has been proposed to add an auxiliary charging material made of cadmium and nickel hydroxide having a specific particle diameter to the active material paste. By adding the nickel hydroxide to the active material paste, the coagulation of cadmium is inhibited and the decrease in discharge capacity is prevented even after repetitive charges and discharges.

[0003]

[PROBLEM THAT THE INVENTION IS TO SOLVE]

However, even if the nickel hydroxide having a specific particle diameter is added to the active material paste, there is a limit to the prevention of the decrease in discharge capacity due to repetitive charges and discharges. The degree of the decrease in discharge capacity is higher than a sintered type alkaline storage battery in which a sintered current collector is filled with an active material.

[0004]

An object of the present invention is to provide a paste type cadmium negative electrode plate for an alkaline storage battery having a long charge/discharge cycle life.

[0005]

Another object of the present invention is to provide an easy method of manufacturing the paste type cadmium negative electrode plate for an alkaline storage battery having a long charge/discharge cycle life.

[0006]

[MEANS FOR SOLVING THE PROBLEM]

The present invention is directed to a paste type cadmium negative electrode plate for an alkaline storage battery comprising a paste type active material added with a nickel compound. According to the present invention, the nickel compound includes a nickel compound which is electrochemically produced from  $\text{Ni(OH)}_2$  as a raw material to

have a nickel valence of 2.2 to 3.4. The "paste type active material" referred herein is an active material prepared by using an active material paste. More specifically, it is a product obtained by filling the active material paste in a current collector and then maturing and drying the filled active material paste. Further, "electrochemically produced" means that the nickel compound is produced by a chemical reaction caused by electric energy. Moreover, the "nickel valence" mentioned herein is a value obtained by dividing a sum of nickel valences of molecules constituting the nickel compound by the number of the molecules. The nickel compound having the nickel valence of 2.2 to 3.4 may be a mixture of  $\text{Ni}(\text{OH})_2$  (nickel valence: 2.0) and  $\text{NiOOH}$  (nickel valence: 3.0), a mixture of  $\text{Ni}(\text{OH})_2$  (nickel valence: 2.0),  $\text{NiOOH}$  (nickel valence: 3.0) and  $\text{NiO}_2$  (nickel valence: 4.0) or a mixture of  $\text{NiOOH}$  (nickel valence: 3.0) and  $\text{NiO}_2$  (nickel valence: 4.0). Where the nickel compound is made of  $\text{Ni}(\text{OH})_2$  (nickel valence: 2.0) and  $\text{NiOOH}$  (nickel valence: 3.0) mixed in the molecular number ratio of 8:2, the nickel valence of the nickel compound is considered to be 2.2. On the other hand, where the nickel compound is made of  $\text{NiOOH}$  (nickel valence: 3.0) and  $\text{NiO}_2$  (nickel valence: 4.0) mixed in the molecular number ratio of 6:4, the nickel valence of the nickel compound is considered to be 3.4. The nickel valence of the nickel compound is easily measured by redox titration with  $\text{KMnO}_4$ .

[0007]

The content of the nickel compound with respect to the paste type active material is preferably 0.05 to 1.0 wt%. If the content is lower than 0.05 wt%, the charge/discharge cycle life cannot be increased to a sufficient degree. On the other hand, if the content is higher than 1.0 wt%, the content of the active material is reduced and the discharge capacity of the battery decreases.

[0008]

In order to prepare a paste type cadmium negative electrode plate for an alkaline storage battery of this kind with ease, first, an unformed electrode plate in which an active material paste added with  $\text{Ni(OH)}_2$  is filled in a current collector is formed. Then, the formed electrode plate is overdischarged such that the nickel valence becomes 2.2 to 3.4. In this way, a desired nickel compound is provided in the active material during the manufacturing process of the negative electrode plate without preparing in advance the nickel compound having the nickel valence of 2.2 to 3.4. Thereby, the negative electrode plate is easily produced.

[0009]

[EFFECT]

When a small amount of the nickel compound which is electrochemically produced from  $\text{Ni(OH)}_2$  as a raw material to have the nickel valence of 2.2 to 3.4 is added to the paste type active material according to the present invention, the charge/discharge cycle life of the battery increases. The

reason for the increase is not specifically clarified.

However, as compared with nickel hydroxide  $[\text{Ni}(\text{OH})_2]$  having a nickel valence of 2.0, the nickel compound having the nickel valence of 2.2 to 3.4 is several times larger in specific surface area and differs in reaction system with an alkaline electrolyte or cadmium. These are considered as contributing to the increase of the cycle life.

[0010]

[EXAMPLES]

(Example 1)

Alkaline storage batteries were produced using negative electrode plates according to this example and negative electrode plates according to the prior art which were different in nickel compound content with respect to the paste type active material. Then, a relationship between the nickel compound content and the number of charge/discharge cycles until the end of life of the battery was observed.

[0011]

The negative electrode plate according to this example was prepared as follows. First, commercially available nickel hydroxide  $[\text{Ni}(\text{OH})_2]$ : nickel valence 2.0] was placed in a bag-shaped nickel container knitted of nickel fibers. Then, the bag-shaped nickel container and a nickel plate were immersed in an aqueous solution of 30 wt% potassium hydroxide. The bag-shaped nickel container was connected to a positive electrode of a power source and the nickel plate was

connected to a negative electrode of the power source. Then, electric current was passed through. The electric current was passed in an amount of 5.8 Ah per 100 g. As a result, part of  $\text{Ni}(\text{OH})_2$  in the bag-shaped nickel container was converted into  $\text{NiOOH}$  (nickel valence: 3.0) to prepare a nickel compound comprising  $\text{Ni}(\text{OH})_2$  and  $\text{NiOOH}$  mixed to have a mean nickel valence of 2.2. This nickel compound was taken out of the bag-shaped nickel container, washed with water and then dried. Then, the nickel compound, 0.5 parts by weight of nylon short fiber, 24 parts by weight of an ethylene glycol solution containing 2 wt% of polyvinyl alcohol and cadmium oxide were kneaded to prepare active material pastes such that the amount of the nickel compound varied from 0 to 3.0 wt% with respect to the paste type active material. The addition amount of the mixture was adjusted by the amount of cadmium oxide. To current collectors made of nickel punched metal, the active material pastes were applied in an amount of 8.0 g, respectively, and then dried to prepare unformed negative electrode plates. The unformed negative electrode plates were charged by a known method to complete negative electrode plates of this example containing the nickel compound in different contents.

[0012]

Negative electrode plates varied in the nickel compound content according to the prior art were prepared in the same manner as the above example except that commercially



available  $\text{Ni}(\text{OH})_2$  having a mean particle diameter of 16  $\mu\text{m}$  and a nickel valence of 2.0 was used in place of the nickel compound in which  $\text{Ni}(\text{OH})_2$  and  $\text{NiOOH}$  were mixed.

[0013]

Each of the negative electrode plates was wound with a known sintered type nickel positive electrode plate and a nylon separator interposed therebetween to prepare a wound electrode plate group. The wound electrode plate groups were combined with an electrolyte containing 30 wt% potassium hydroxide, respectively, to prepare AA type sealed alkaline storage batteries.

[0014]

Each of the batteries was charged at 1  $\text{cmA}$  for 90 minutes and discharged at 1  $\text{cmA}$  to a terminal voltage of 1.0 V. This charge/discharge was repeated to count the number of charge/discharge cycles until the capacity becomes 70 % of the initial capacity (the number of charge/discharge cycles until the end of the battery life). Thus, a relationship between the addition amount of the nickel compound and the number of charge/discharge cycles until the end of the battery life was observed with respect to the batteries using the negative electrode plates according to the example and the batteries using the negative electrode plates according to the prior art. FIG. 1 shows the observation results. Referring to this figure, the batteries using the prior art negative electrode plates (nickel valence: 2.0) reached their end of life at

about 600 cycles. On the other hand, the batteries using the negative electrode plates according to the example (nickel valence: 2.2) showed the effect when the nickel compound content was 0.05 wt% and increased their life to about 800 cycles when the nickel compound content was 0.5 wt%.

[0015]

(Example 2)

Next, various nickel compounds having the nickel valence of 2.2, 2.8, 3.0 and 3.4, respectively, were made by varying the current-running time. Thereafter, in the same manner as the above example, negative electrode plates having different nickel valences were prepared and batteries using the negative electrode plates, respectively, were made. The addition amount of the nickel compound to the paste type active material was 0.5 wt%. Charges and discharges were repeated in the same manner as Example 1 to observe a relationship between the nickel valence and the number of charge/discharge cycles until the end of the battery life. FIG. 2 shows the observation results together with the result of a battery using the negative electrode plate having a nickel valence of 2.0 (prior art negative electrode plate). Referring to this figure, the battery using the prior art negative electrode plate having the nickel valence of 2.0 reached its end of life at about 600 cycles. On the other hand, the batteries using the negative electrode plates having the nickel valence of 2.2 or more increased their life to

about 800 cycles.

[0016]

(Example 3)

Various negative electrode plates having different nickel valences were produced in a different manner from Example 1 and a relationship between the nickel valence and the number of charge/discharge cycles until the end of the battery life was observed. First, 0.5 parts by weight of commercially available nickel hydroxide  $[\text{Ni}(\text{OH})_2]$ : nickel valence 2.0], 0.5 parts by weight of nylon short fiber, 24 parts by weight of an ethylene glycol solution containing 2 wt% of polyvinyl alcohol and 75 parts by weight of cadmium oxide were kneaded to prepare an active material paste. Then, 8.0 g of the active material paste was applied to current collectors made of nickel punched metal and dried to prepare unformed negative electrode plates. The unformed negative electrode plates were formed in a 30 wt% potassium hydroxide solution to obtain formed negative electrode plates. Then, at 0.2 cmA relative to the capacity of the formed negative plates, one of the formed negative electrode plates was completely discharged and the other were overdischarged at the same current for 10 minutes, 30 minutes and 60 minutes, respectively. The complete discharge and the overdischarge were carried out by a so-called forced discharge in which the positive and negative electrodes were connected inversely to a power source. In the complete discharge mentioned herein,

discharge is carried out to the amount corresponding the capacity of cadmium as the negative electrode active material and then the discharge is stopped at a terminal voltage. Due to the overdischarge after the complete discharge, part of  $\text{Ni(OH)}_2$  was converted to  $\text{NiOOH}$  or  $\text{NiO}_2$  and the nickel valence became 2.3, 2.5 and 3.1 after the overdischarge for 10 minutes, 30 minutes and 60 minutes, respectively. Then, batteries having different nickel valences were repetitively charged and discharged under the same conditions of Example 1 to observe a relationship between the nickel valence and the number of charge/discharge cycles until the end of the battery life. FIG. 3 shows the observation results. Referring to this figure, the battery using the prior art negative electrode plate (nickel valence: 2.0) which was not overdischarged reached its end of life at about 400 cycles. On the other hand, the batteries using the overcharged negative electrode plates increased their charge/discharge cycle life. This is because of the valence of the added nickel hydroxide increased higher than 2.0.

[0017]

Hereinafter, among the inventions described in the specification, several ones are explained.

[0018]

(1) A paste type cadmium negative electrode plate for an alkaline storage battery comprising a paste type active material filled in a current collector and a nickel compound

added to the paste type active material, wherein the nickel compound includes a nickel compound in which  $\text{Ni(OH)}_2$ ,  $\text{NiOOH}$  and  $\text{NiO}_2$  which are electrochemically produced from  $\text{Ni(OH)}_2$  as a raw material are mixed to have a nickel valence of 2.2 to 3.4, and the content of the nickel compound with respect to the paste type active material is 0.05 to 1.0 wt%.

[0019]

(2) A method of manufacturing a paste type cadmium negative electrode plate for an alkaline storage battery comprising filling an active material paste added with a nickel compound in a current collector, wherein the nickel compound is prepared by immersing a bag-shaped nickel container made of nickel fibers containing  $\text{Ni(OH)}_2$  powder and a nickel plate into a potassium hydroxide aqueous solution, connecting the bag-shaped nickel container to a positive electrode of a power source and the nickel plate to a negative electrode of the power source and discharging until the nickel valence of nickel in the bag-shaped nickel container reaches 2.2 to 3.4.

[0020]

(3) A method of manufacturing a paste type cadmium negative electrode plate for an alkaline storage battery comprising filling an active material paste added with  $\text{Ni(OH)}_2$  in a current collector, wherein an unformed electrode plate in which an active material paste added with  $\text{Ni(OH)}_2$  is filled in a current collector is formed, the formed electrode plate is

subjected to complete discharge by force discharge and then subjected to overdischarge by force discharge at the same current as that for the complete discharge until the nickel valence reaches 2.2 to 3.4.

[0021]

[EFFECT OF THE INVENTION]

According to the present invention, a substance which is produced electrochemically from  $\text{Ni}(\text{OH})_2$  as a raw material to have a nickel valence of 2.2 to 3.4 is used as a nickel compound. Therefore, by adding a small amount of the nickel compound to a paste type active material, charge/discharge cycle life of a battery is increased.

[BRIEF EXPLANATION OF THE DRAWINGS]

[FIG. 1] A graph showing a relationship between the nickel compound content in the battery examined and the number of charge/discharge cycles until the end of the battery life.

[FIG. 2] A graph showing a relationship between a nickel valence of a nickel compound contained in a negative electrode plate and the number of charge/discharge cycles until the end of the battery life.

[FIG. 3] A graph showing a relationship between overdischarging time for the battery after formation and the number of charge/discharge cycles until the end of the battery life.

Fig. 1

【図1】

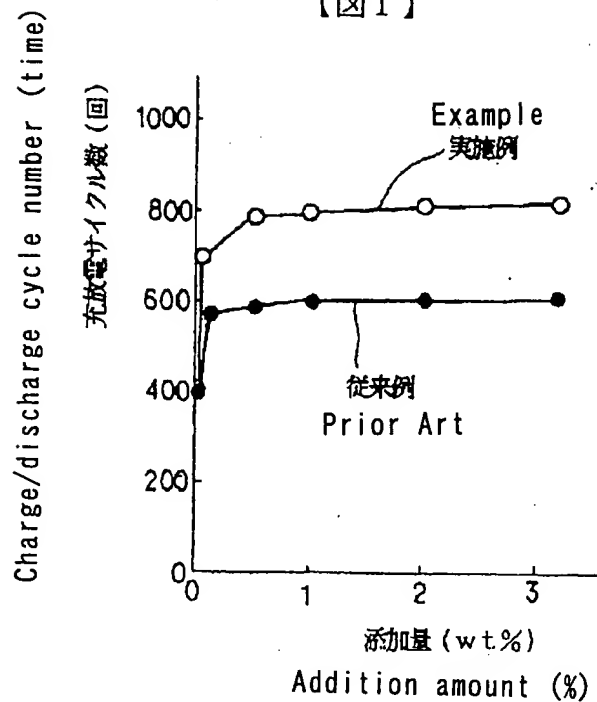


Fig. 2

【図2】

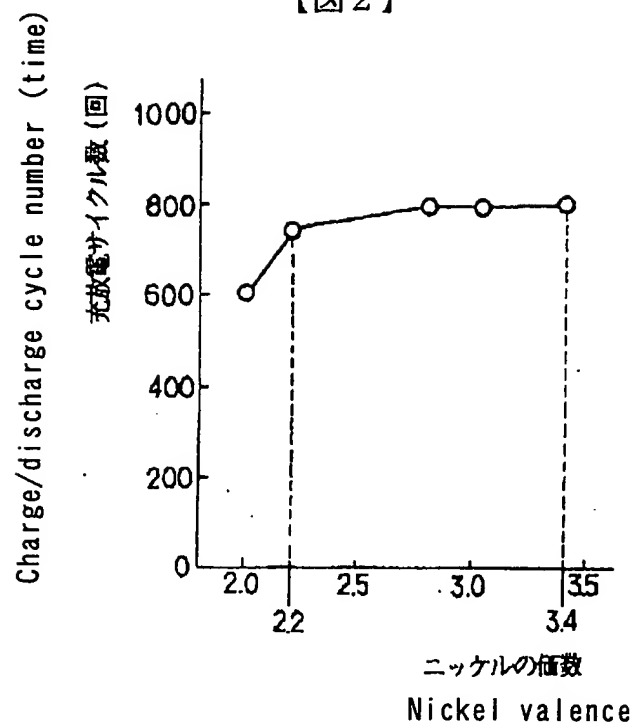


Fig. 3

【図3】

